

Fate and Transport of Ethanol in the Environment

**Presented to the Environmental Protection
Agency Blue Ribbon Panel**

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Outline

- ▲ **Properties**
- ▲ **Fate and Transport**
- ▲ **Biological Field / Lab Studies**
- ▲ **Impact on BTEX Plume Lengths**
- ▲ **Remediation and Treatment**
- ▲ **Conclusions**
- ▲ **Research Needs**

Objectives

- ▲ The fate and transport of ethanol in the environment is well understood; however, the interactions between ethanol and other gasoline constituents and their resulting fate and transport is not well understood.
- ▲ Our objectives are to assess the likely fate and transport of ethanol in the soil and water within a range of geochemical conditions.

Production and History of Use

- ▲ **94% of Ethanol produced from corn fermentation**
- ▲ **Ethanol must be denatured prior to use**
 - addition of 2% to 5% of approved denaturant
- ▲ **In 1998, 15% of all oxygenated gasoline contained ethanol**
 - 5.4% by volume ethanol corresponds to 2% by weight oxygen
 - Ethanol commonly added up to 10% by volume
 - Oil companies in Brazil use 24% ethanol by volume

Key Questions

- ▲ What is the fate of constituents of concern in gasoline following an ethanol release to the subsurface?
- ▲ What is the fate of ethanol following release to surface water?
- ▲ What is the impact of gasoline releases with ethanol on existing plumes - BTEX or MTBE?

Comparative Properties of Ethanol and Other Gasoline Additives

| Property (@ 25°C) | MTBE | Benzene | Ethanol |
|---|-------------|-------------|---------------|
| Vapor Pressure [mm HG] | 245 | 95 | 49 - 56 |
| Reid Vapor Pressure (38°C) [psi] | 7.8 | 2 | 18 |
| Solubility [mg/l] | 43,000 | 1,780 | miscible |
| Henry's Constant [-] | 0.02 | 0.22 | 0.000252 |
| Log K _{ow} | 1.1 - 1.2 | 1.56 - 2.15 | -0.16 - -0.32 |
| California Drinking Water Maximum Contaminant Level [ppb] | 5 (SMCL) | 1 (MCL) | NA |
| % Used in Reformulated Gasoline | 11 – 15% | < 1% | 5% - 10% |

Significance of Properties

▲ Properties

▲ Examples of Significance

- | | | |
|---------------------------------------|--------|--|
| – Aqueous Solubility | —————→ | Rate of migration; bioavailability |
| – Vapor Pressure | —————→ | Volatilization from LNAPL; Soil vapor extraction |
| – Henry's Constant | —————→ | Volatilization from water; Air stripping |
| – Octanol/Water Partition Coefficient | —————→ | Rate of migration; Adsorption Potential |
| – Biodegradability | —————→ | Plume size; in-situ biodegradation |
| – Reactivity | —————→ | Oxidation potential |
| – Structure | —————→ | Biodegradability; oxidation potential |

Aqueous Solubility

▲ Raoult's Law (holds for low contaminant concentrations)

$$C_{gw} = Sol_{theoretical} X_{gasoline}$$

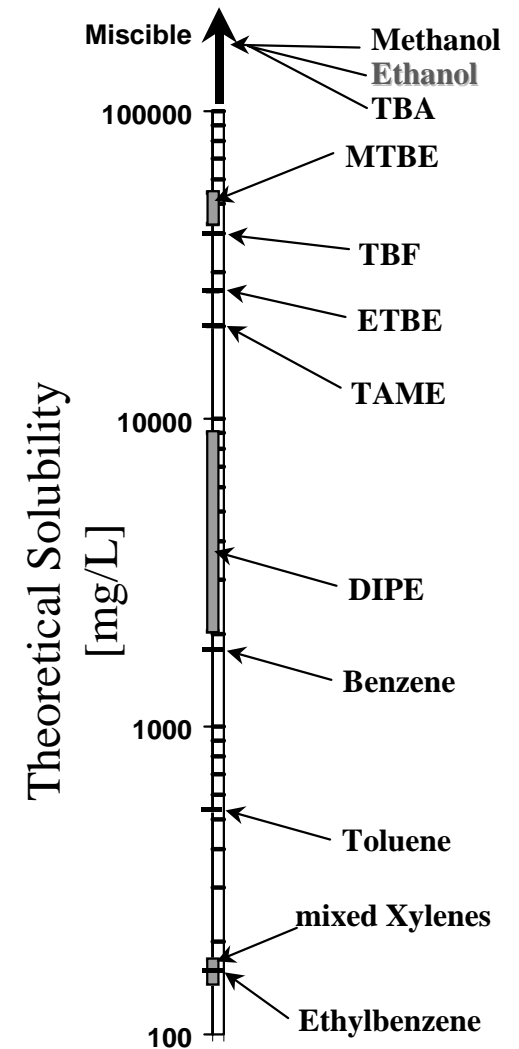
- $C_{MTBE,gw} \cong (48,000 \text{ ppm})(11\%) = 5,280 \text{ ppm}$
- $C_{benzene,gw} \cong (1,750 \text{ ppm})(1\%) = 17.5 \text{ ppm}$

▲ Does not hold for miscible contaminants (e.g. ethanol, TBA, methanol)

- $C_{ethanol,gw} \cong \frac{C_{ethanol,gasoline}}{MixingRatio * DilutionRatio}$
- Actual source area ethanol concentrations higher than MTBE. i.e., <1,000 ppm

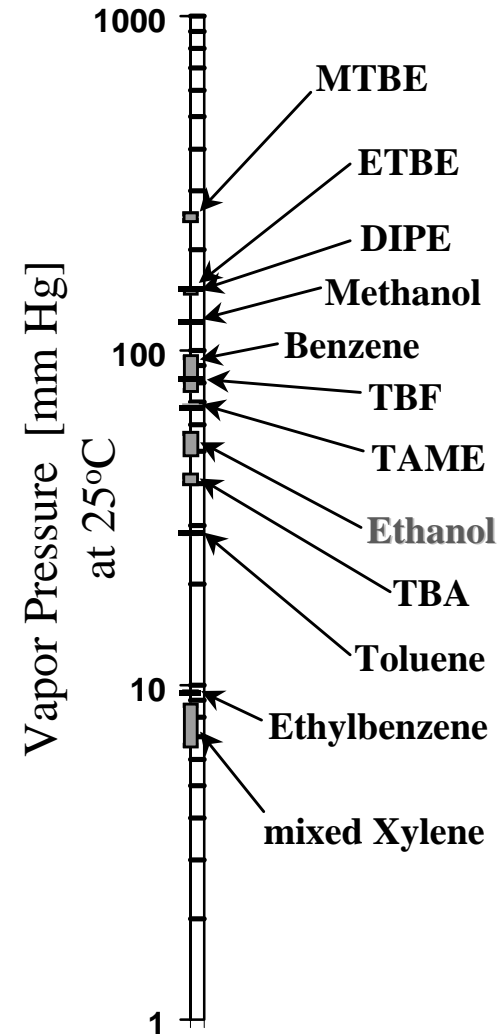
▲ High solubility (> 10,000 mg/L)

- Fast dissolution
- Lower sorption
- Potential cosolvency effect



Vapor Pressure (mm Hg)

- ▲ As pure ethanol - low vapor pressure
- ▲ In hydrocarbon plume - non-ideal behavior - highly polar
 - Much higher effective vapor pressure
 - Reid vapor pressure (18 psi) greater than MTBE (8 psi) or benzene (2 psi)
 - greater tendency to volatilize



Henry's Law Constant (H)

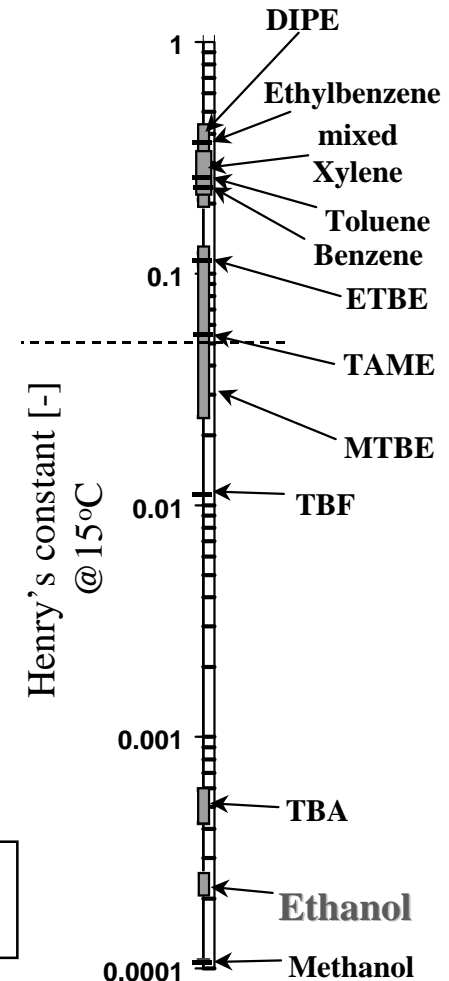
▲ Ethanol Henry's Constant = 0.000252

▲ Henry's Constant < 0.05

- Volatilization from surface waters unlikely
- Off-gassing from groundwater unlikely
- Vapor phase retardation will be high

$$H \text{ [(atm-m}^3\text{)/(mole)]} / RT = H[-]$$

$$R = 0.08206 \text{ [(atm-m}^3\text{)/(mole-K)]; } T = [^{\circ}\text{K}] = ^{\circ}\text{C} + 273$$



Log K_{oc}

$$R = 1 + \frac{f_{oc} K_{oc} \rho_{bulk}}{\eta}$$

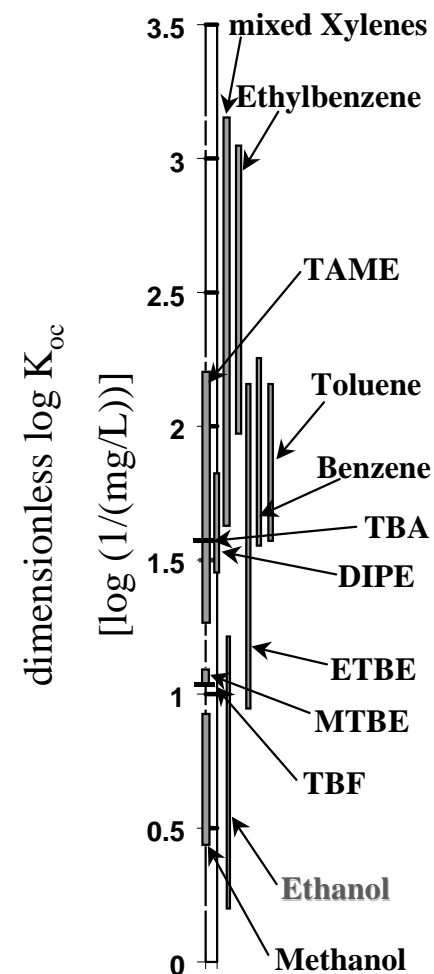
$$R = 1 + \left(\frac{\theta_w}{\theta_a} \frac{1}{H} \right) + \left(\frac{f_{oc} K_{oc} \rho_{bulk}}{\theta_a H} \right)$$

- ▲ Increasing K_{oc} increases retardation (R) for constant soil properties

$$\frac{R_{benzene}}{R_{MTBE}} \cong 4.5$$

$$\frac{R_{ethanol}}{R_{MTBE}} \cong 0.25$$

- ▲ As R approaches unity, contaminant moves at speed of groundwater



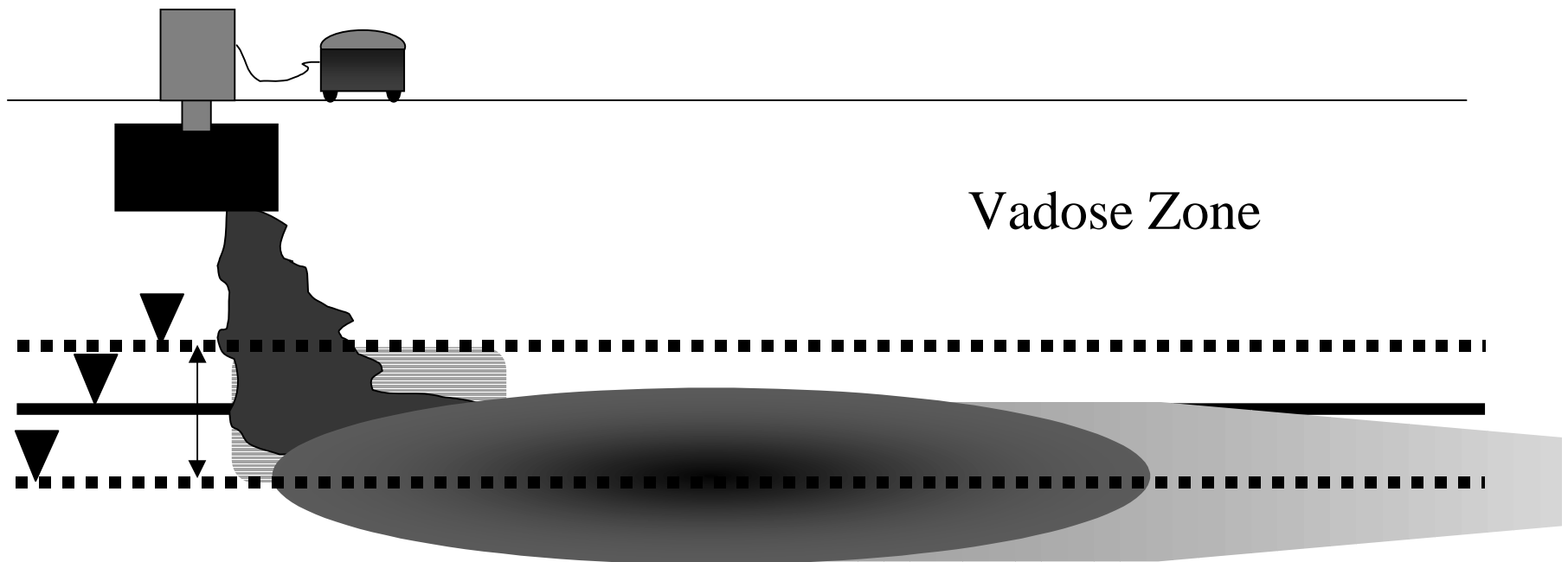
BTEX Plume Elongation: Possible Causes

- ▲ Increase in aqueous solubility of BTEX due to high ethanol concentration in water**
- ▲ Preferential utilization of ethanol**
- ▲ Larger volume of groundwater under anaerobic conditions; shift to methanogenic redox conditions.**

Cosolvency of Ethanol

- ▲ **Dependent on ethanol concentration in groundwater**
 - function of dilution factors
 - concentration drops with distance from source
- ▲ **Corseuil (1998) found ethanol concentrations >10,000 ppm will increase BTEX solubility**
- ▲ **Ethanol 10% in gasoline with 5-fold dilution factor results in groundwater concentrations of 20,000 ppm**

Conceptual Model of BTEX Plume Elongation



Biodegradation of Ethanol

- ▲ **Limited field studies to date**
- ▲ **Expected to rapidly biodegrade in groundwater and surface water**
- ▲ **Toxic at high concentrations (>100,000 ppm)**
- ▲ **One known methanol field study**
 - Borden Field Site: half-life = 40 days
- ▲ **Numerous microcosm laboratory studies of ethanol**
 - Corseuil shows 80-100 mg/L degrading rapidly
 - Aerobically - 5 days
 - Anaerobically - 12 to 25 days

Summary of Literature Biodegradation Rates

| Compound | Anaerobic Pseudo First Order Rate Constant | |
|----------|--|-------------------------------------|
| | Electron Acceptor | Range of Rates (day ⁻¹) |
| Ethanol | NO ₃ ⁻ | 0.53 ^(1*) |
| | Fe ³⁺ | 0.17 ^(1*) |
| | SO ₄ ⁻² | 0.1 ^(1*) |
| | Anaerobic Range | 0.0062 - 0.00096 ^(3**) |
| Benzene | NO ₃ ⁻ | 0-0.045 ^(2*) |
| | Fe ³⁺ | 0-0.024 ^(2*) |
| | SO ₄ ⁻² | 0-0.047 ^(2*) |
| | Methanogenic | 0-0.052 ^(2*) |
| | General | 0.0062-0.00096 ^(3**) |

1) Estimated from Corseuil et. al., 1997; 2) Aronson et. al., 1997; 3) USGS, 1998; 4) Barker et. al., 1998;

*Determined in a laboratory;

** Estimated from first principles.

Ethanol Effect on BTEX Degradation

▲ Corseuil et al., 1998

- Ethanol retarded BTEX aerobic biodegradation in laboratory; rapidly reduced oxygen concentrations
- No benzene degradation observed under anaerobic conditions
- Ethanol slowed toluene anaerobic degradation

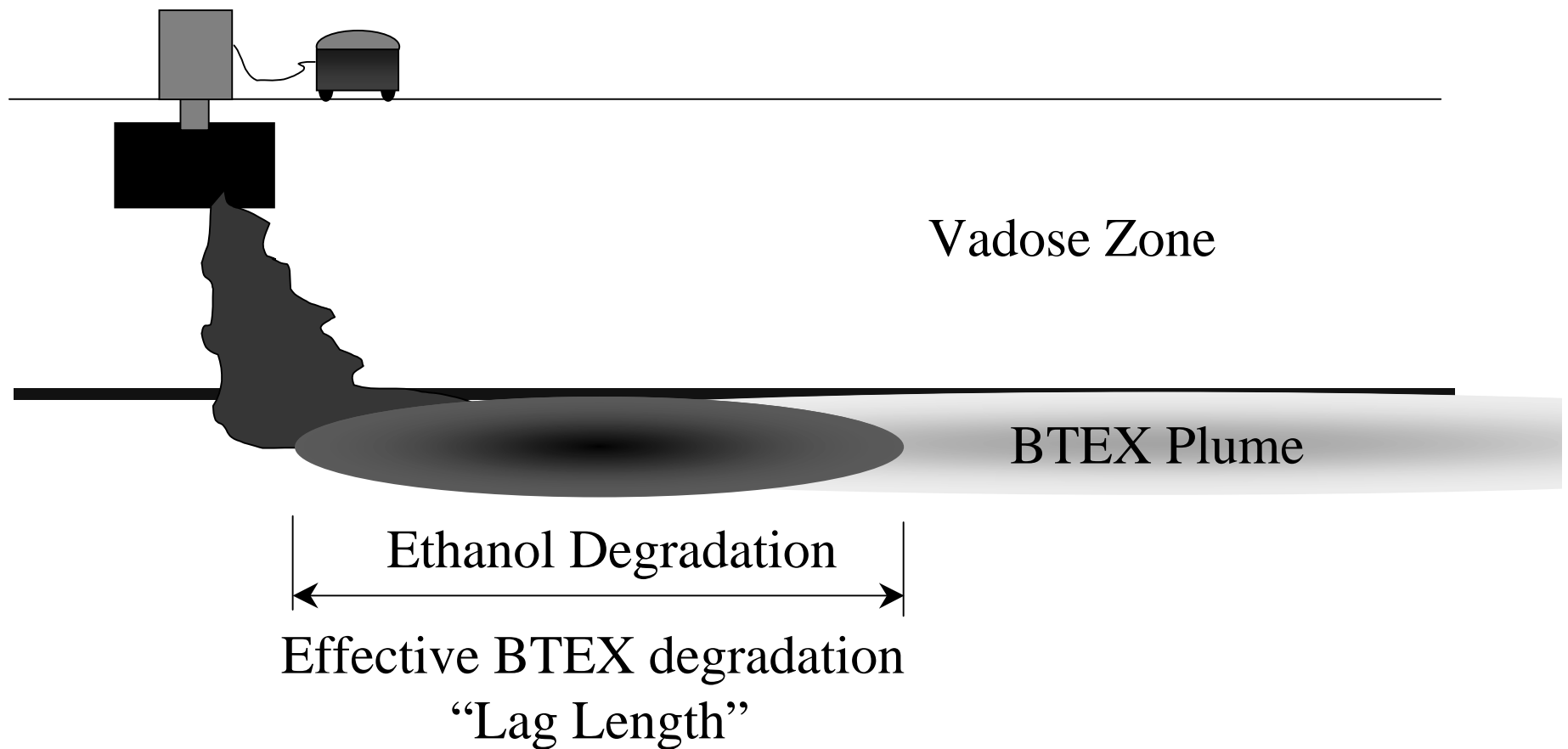
▲ Hunt et al., 1997

- Degradation of toluene completely inhibited until all the ethanol was degraded (aquifer microcosm)

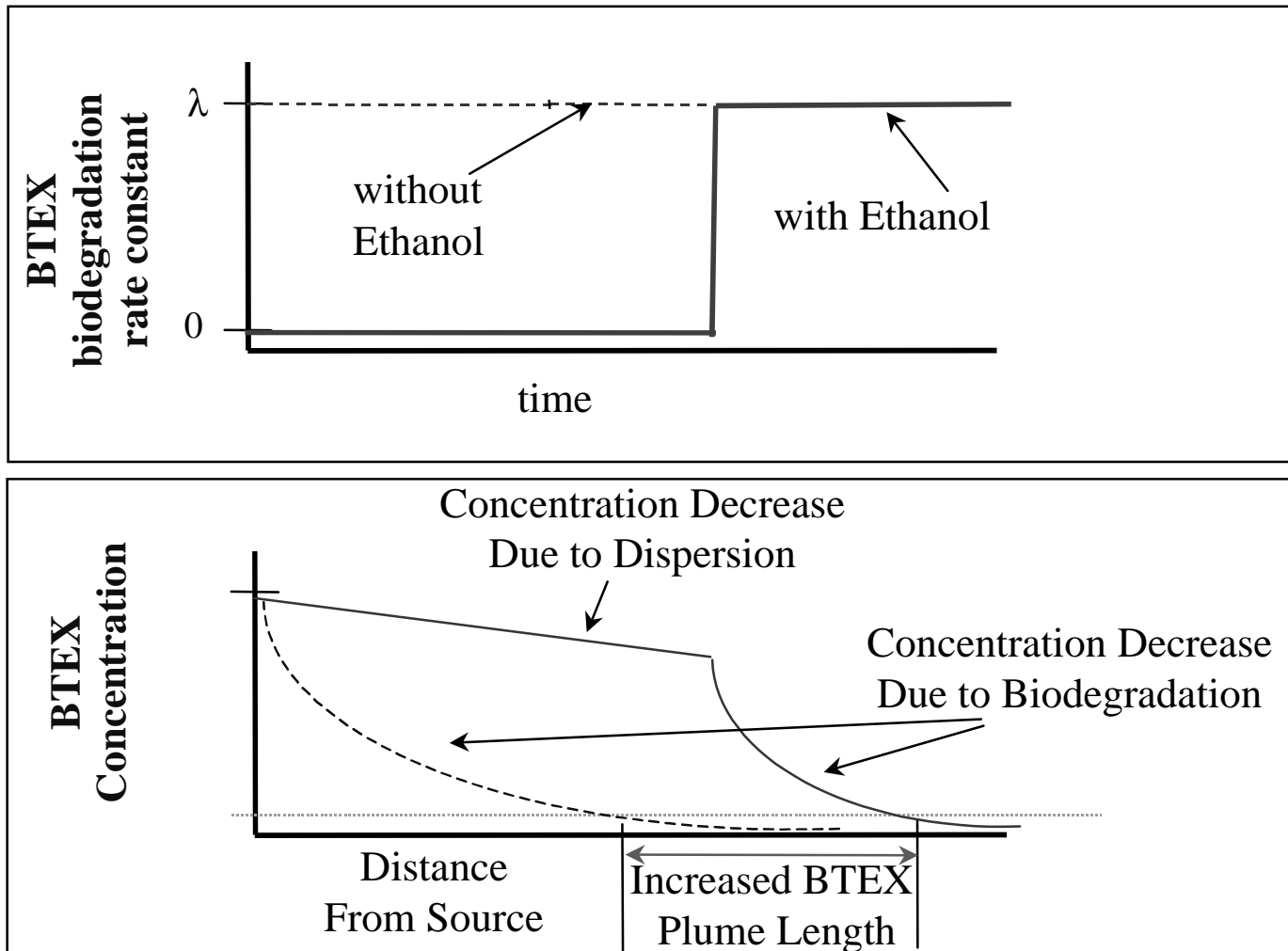
▲ Barker et al., 1990

- Methanol inhibits degradation of BTEX due to initial toxic levels; later due to depletion of electron acceptors

Conceptual Model of BTEX Plume Elongation



Conceptual Model



Modeling Assumptions

- ▲ Modeled the degradation of benzene with and without ethanol present
- ▲ Alkane interactions and degradation were not considered
- ▲ Source area ethanol concentrations were assumed to be 4000 ppm (assumes 20-fold dilution)

Modeling Assumptions (cont.)

▲ 2-D Domenico Analytical Model includes:

- first order decay rate
- advection
- retardation
- dispersion

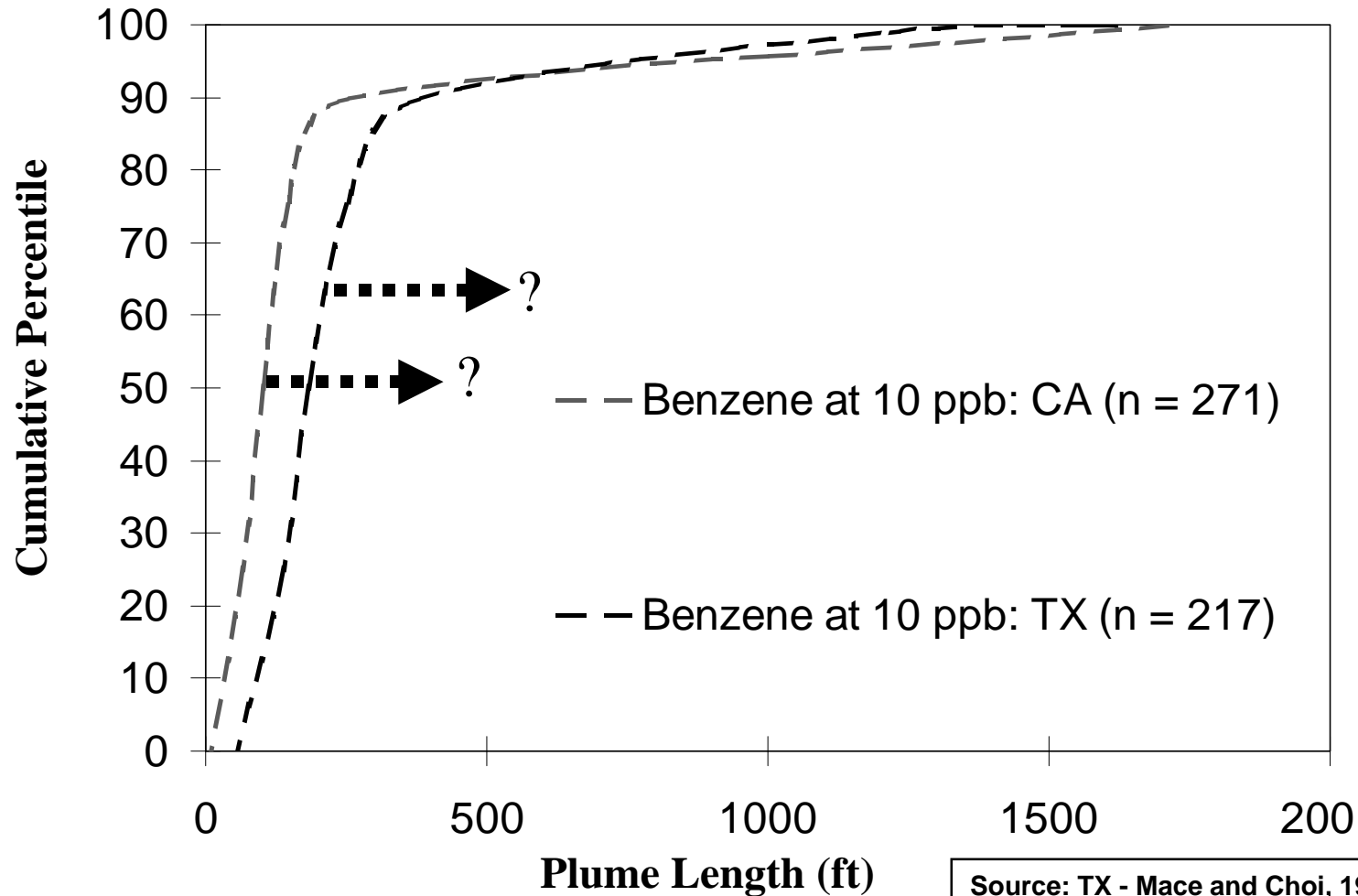
▲ Sensitivity Analysis of subsurface variables

- groundwater velocity: 0.004 - 0.4 feet/day
- organic carbon content: 0.01 - 0.005

Results

- ▲ **Typical BTEX plumes in California and Texas travel no further than 300 ft from source**
- ▲ **Addition of ethanol to gasoline may extend BTEX plumes by 25% to 40%**
- ▲ **Higher source area ethanol concentrations would suggest a larger effect**

Historical Benzene Plume Lengths



Technical Options for Remediation and Treatment of Ethanol

Possible Remediation

- ▲ Soil Vapor Extraction (SVE)
- ▲ Soil Heating/SVE
- ▲ Pump and Treat
- ▲ Air Sparging /SVE
- ▲ Multiple Phase Vacuum Extraction

Possible Treatment

- ▲ Steam Stripping
- ▲ Advanced Oxidation
- ▲ Resins

Proven Remediation

- ▲ Biological Degradation

Possible Treatment

- ▲ Biological activated filter

Conclusions

- ▲ **Ethanol is miscible in water; does not adsorb nor volatilize**
 - High potential source area concentrations
- ▲ **Ethanol will rapidly biodegrade following release to the environment**
 - rapid depletion of electron acceptors
 - suspected interference with hydrocarbon biodegradation
- ▲ **Ethanol is preferentially biodegraded compared to other gasoline constituents (e.g., benzene, MTBE)**
- ▲ **If ethanol enters a drinking water supply, ex-situ remediation will be difficult**

Data Gaps and Unknowns

- ▲ **Occurrence of ethanol in water in states using gasohol (MTBE Research Partnership)**
- ▲ **Impact of ethanol on BTEX plumes**
 - cosolvency (Corseuil, et al., 1999)
 - plume elongation (Corseuil, et al., 1999)
- ▲ **Impact on costs of site characterization and remediation**
- ▲ **Impact of ethanol on MTBE plumes**
- ▲ **Toxicity of ethanol in source area**
 - fate of pure ethanol spill (Buscheck, Chevron)
- ▲ **Treatment of ethanol-impacted drinking water (MTBE Research Partnership)**